Diversely Halogenated Spiropyrans - Useful Synthetic Building Blocks for a Versatile Class of Molecular Switches

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Abstract

Spiropyrans are dyes that can be reversibly switched to a highly colored merocyanine form by a number of stimuli such as light, mechanical force or temperature. To make use of these molecules, there is a requirement to functionalize them appropriately. Herein we report a library of spiropyrans bearing two (pseudo)halide functional groups on either half of the molecule. Such halide substituents are valuable, because they themselves may be used as reactive sites in cross-coupling reactions, for example. Different combinations of halides, for which different reactivities in cross-coupling reactions may be expected, will facilitate selective consecutive cross-coupling reactions and condensations. Data concerning the UV-vis characteristics, the photostationary equilibria of the materials as well as the half-life of the merocyanine forms in solution are presented.

Highlights

- Versatile synthesis of 8 new spiropyrans with bromide, iodide and hydroxy functions
- Transformation from hydroxy to OTf functional groups on spiropyrans (5 examples).
- UV/vis characterization of 13 new spiropyran dyes in terms of PSS and half-life times
- ^{1}H NMR analysis of the ratio between two switching states at dark conditions and low concentrations

Keywords

Molecular switch; spiropyran; organic synthesis; *3H*-indole; photochromism

1. Introduction

Molecular switches are molecules that can exist in two or more metastable states. They can be transformed from one state into the other by applying external stimuli such as changes in pH, irradiation with light or by mechanical force.[1–3] Molecular switches are therefore instrumental for the development of new “intelligent” materials,[4] or molecular machines.[5] Spiropyrans belong to the most important molecular switches, because of the exceptionally large variety of diverse stimuli that can be used for switching: Their isomerization between a closed spiropyran form and an open merocyanine form can be induced by light,[6] pH,[7–10] the presence of ions,[11–13] pressure,[14] mechanical force[1,2,14–21] as well as electric fields.[19,22] Of those stimuli, the light induced switching provides to be easily accessible and nondestructive. In addition, the absorption coefficient for the merocyanine forms is extremely high (ca. 45,000 $Lmol^{-1}cm^{-1}$ at 550 nm)[23] so that only very low concentrations of switches have to be present to detect switching events visually (Figure 1).

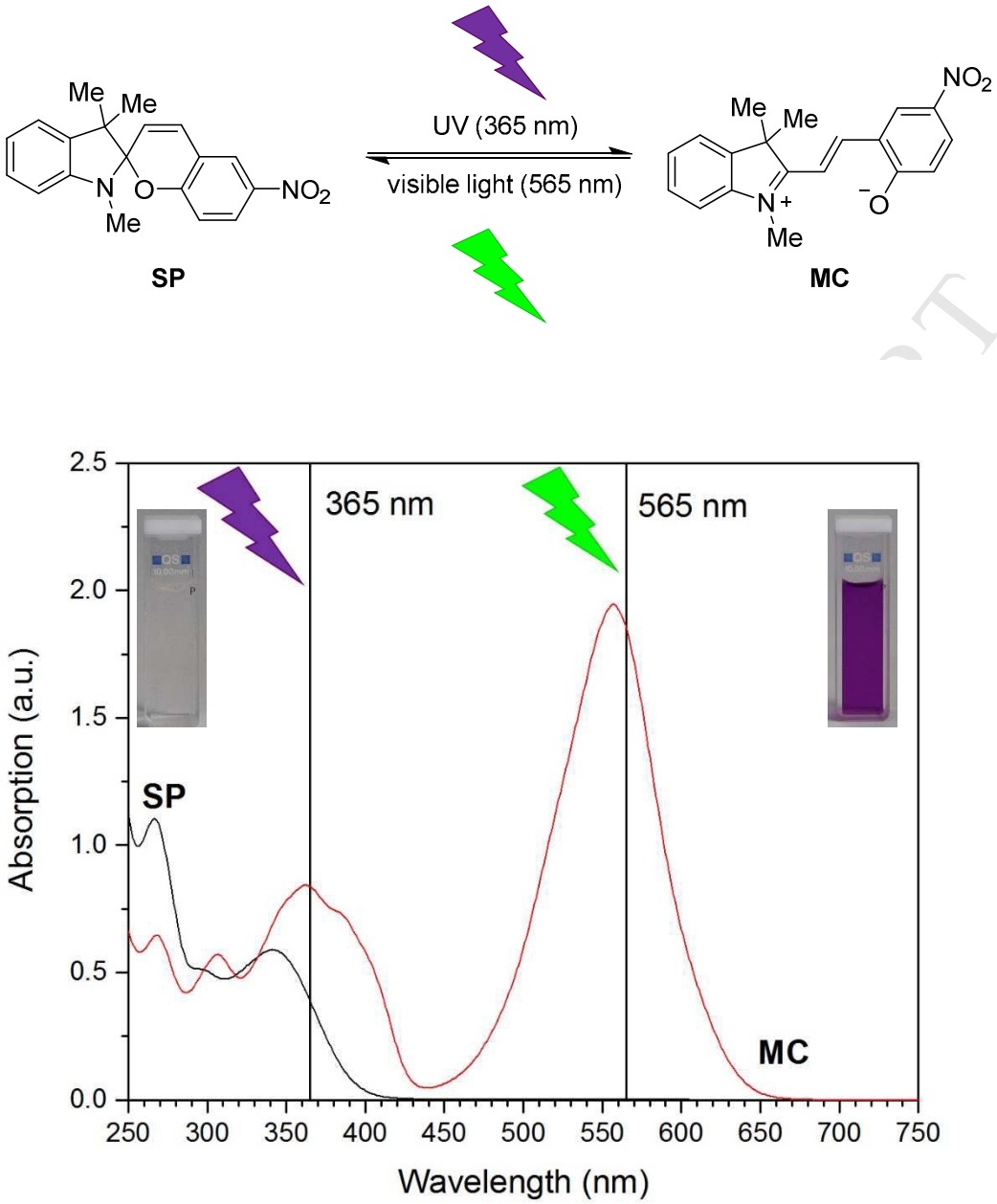


Figure 1: top: Switching states of spiropyrans. The closed spiropyran form (**SP**) undergoes a ring opening upon irradiation with UV light (365 nm, purple flash) to the open merocyanine form (**MC**). Irradiation with visible light (565 nm, green flash) induces a ring closure and drives the equilibrium towards the **SP** side. Bottom: Absorption spectra and photographs of the two states. The absorption spectrum of the **SP** is plotted in black, the spectrum of the **MC** in red. Flashes and vertical lines represent the wavelengths used for switching. Whereas the colorless SP form does not absorb at wavelengths higher than 400 nm, the solution of **MC** shows a dark purple color which results from a broad absorption with a maximum wavelength of approx. 550 nm. The solution in acetonitrile had a concentration of 65 µmol/L and irradiation times of 30 sec were used.

The photochemical properties of the open merocyanine form, with its closed ring systems connected by an sp3 carbon centre, are in striking contrast to the properties of the spiropyran.

Whereas spiropyrans consist of two separated π-electron systems and therefore absorb only in the UV region of the spectrum, merocyanines possess one planar π-system. In this π-system, the electrons are delocalized across the entire molecule, which causes a broad absorption maximum at ca. 550 nm. Irradiation with light of wavelengths that correspond to the absorption maxima leads to a decrease in the concentration of the irradiated species. Therefore, UV irradiation induces the ring opening, whereas visible light facilitates the ring closure. (Figure 1)

Since 2007, spiropyrans have been used as mechanophores.[6] Therefore, they represent a relatively rare class of molecules in which a mechanical force induces a chemical transformation. Because spiropyrans are also chromophores, it is possible to visualize the switching event. The mechanical rupture of the bond between the spiro carbon atom and the oxygen atom can be induced by grinding of the solid spiropyran.[2] The use of spiropyrans as mechano active sensors in materials (such as polymers) requires a covalent connection of the mechanophore to polymeric chains.[1] This construction principle enables the material to respond to stretching or compression by a color change.[6]

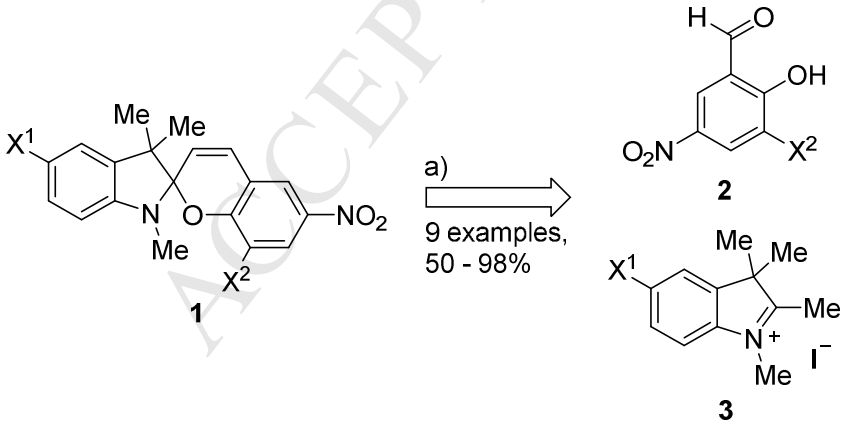
Thus, mechanical forces applied to the periphery of the molecule are being transferred to the central bond. DFT calculations suggest a functionalization of the spiropyran at both, the chromene and the indole side, which was confirmed experimentally.[14] However, the possibilities to access these two positions are very limited. To date, a covalent incorporation of spiropyrans to the backbones of polymers was achieved by six methods: electropolymerization,[24] introduction of an ATRP initiator by ester condensation to a phenolic spiropyran, followed by radical polymerization,[18] polyurethane (PU) formation,[17] hydrosilation,[19] ring-opening polymerization (ROP) with ε-caprolactone,[15] ring-opening metathesis polymerization (ROMP),[21] and polycondensation by Suzuki coupling.[25–27] The incorporation into polysiloxanes by hydrosilation as well as the usage of ATRP, ROP or

ROMP methods or polycondensations to form PU use hydroxyl groups at the spiropyran. In contrast, due to a limited availability of spiropyrans with halide functions, very few examples of functionalization of spiropyrans by cross coupling have been reported.[25–27] Especially the differentiating functionalization of the two halves of the molecule (indoline and chromene) with groups of different reactivity promises a broader variety of options for further functionalizations and thus a wider applicability of spiropyrans.

Therefore, to make spiropyrans amenable as electrophiles in cross coupling reactions, a library of spiropyrans was synthesized that contained several substitution patterns of bromide, iodide and trifluoromethanesulfonyl as leaving groups.

2. Experimental Part[1]

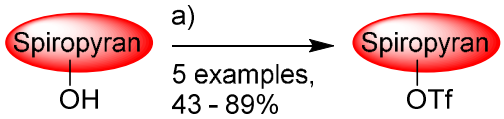
Spiropyrans **1** are typically synthesized by a condensation reaction of a Fischer's base and a salicylaldehyde **2** (Scheme 1, section 2.2.1).[28] The Fischer's base is released *in situ* from an indolium salt **3** under basic conditions. To establish a general procedure (9 examples) for the versatile functionalization of spiropyrans, it was crucial to synthesize these precursors **2** (section 2.1.1) and **3** (section 2.1.2) bearing the desired functional groups, halides and hydroxides.



Scheme 1: Synthetic overview of the syntheses of spiropyrans with X^1 and X^2 = Br, I, OH. a) ethanol, piperidine (2 eq.), reflux, yields varying from 50 – 98%.

[1] Further information concerning the used chemicals (supplier, purity, and purification procedures), equipment and experimental data (detailed procedures, purification, characterization, NMR spectra) are provided in the supporting material.

The hydroxy groups were to be converted into trifluoromethylsulfonates after the spiropyran formation (Scheme 2). Therefore, we established a versatile synthesis (5 examples) using trifluoromethylsulfonic anhydride as electrophile in DCM / pyridine as solvent / base system under a nitrogen atmosphere (section 2.2.2).



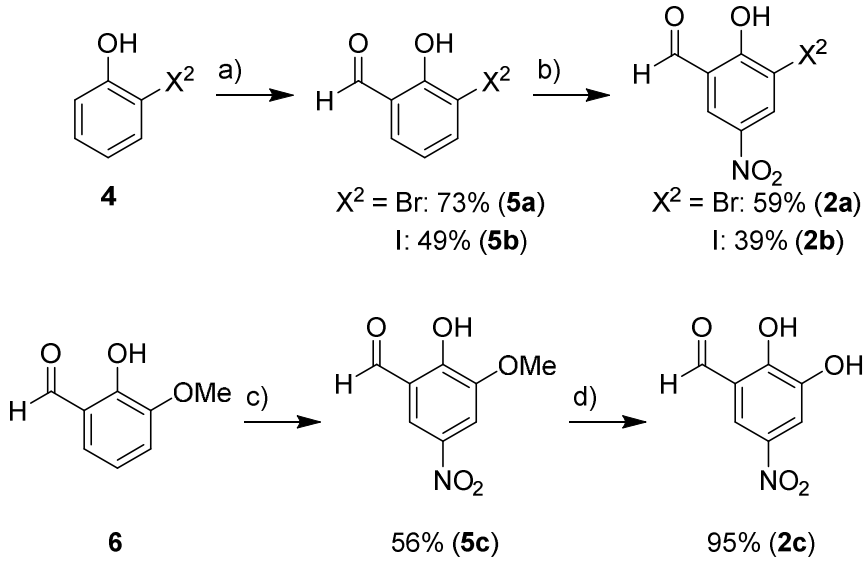
Scheme 2: Introduction of trifluoromethylsulfonates. a) Tf_2O, pyridine, DCM, 0 – 40 °C.

2.1. Syntheses of the Precursor Molecules

2.1.1. Salicylaldehyde Derivatives

The 3-halide-5-nitrosalicylaldehydes (**2a** and **2b**) were synthesized in a two-step reaction sequence, starting from 2-halide phenol **4** (Scheme 3). By a magnesium (II) directed *ortho*-formylation with paraformaldehyde, the aldehyde functions were selectively introduced in moderate to good yields of 73% (X^2 = Br) or 49% (X^2 = I, Lit. 84%[29]) to obtain the salicylaldehydes **5a** and **5b**. The procedure for the synthesis of the 2-hydroxy-3-iodobenzaldehyde was reported before[29] and could be adapted for the synthesis of the bromo functionalized species. A *meta*-selective nitration was performed to prepare the nitrosalicylaldehydes **2a** and **2b** in moderate yields of 59% (X^2 = Br) or 39% (X^2 = I). An equimolar amount of fuming nitric acid in acetic acid was used as nitrating agent.

The synthesis of 3-hydroxysalicylaldehyde (**2c**) started from *ortho*-vanillin (**6**).[14]. First, the nitro group was introduced using fuming nitric acid in acetic acid as nitrating agent in a yield of 56% (Lit. 50%[14]). Afterwards, the methoxy group was transferred into a hydroxy group using hydrobromic acid in an excellent yield of 95% (Lit. 86%[14]).



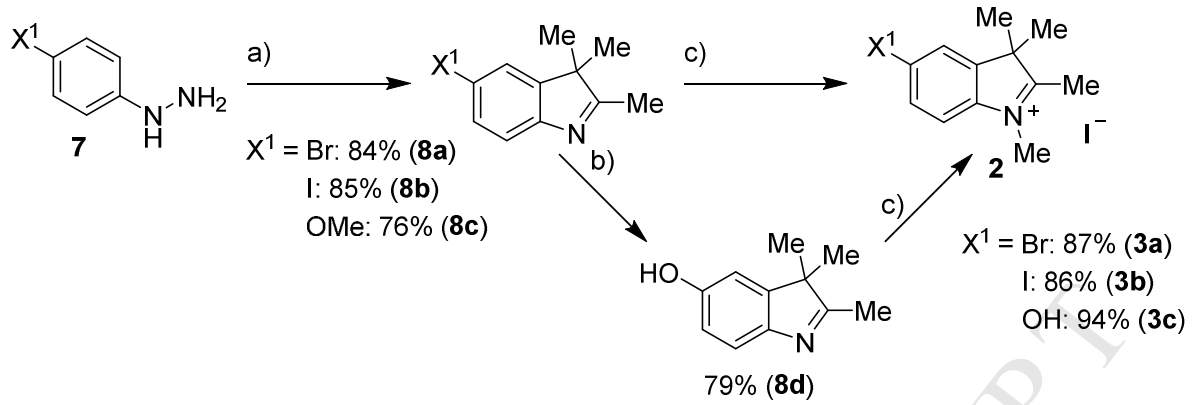
Scheme 3: Synthetic routes to obtain the salicylaldehyde precursors. a) paraformaldehyde, magnesium chloride, trimethylamine, THF, reflux. b) nitric acid / acetic acid, 15-25 °C. c) nitric acid in acetic acid, 15 °C. d) hydrobromic acid, reflux. Overall yields: X^2 = Br: 43%, X^2 = I: 19%, X^2 = OH: 53%.

2.1.2. Indolium Salts

The indole species were prepared as indolium iodide salts **3a-c** in a linear synthetic route, starting from 1,4-substituted phenyl hydrazines **7** (Scheme 4). It was possible to prepare the trimethyl-*3H*-indoles bearing bromide (**8a**), iodide (**8b**) and methoxy (**8c**) substituents at the 5-position *via* a Fischer indole synthesis in good yields ranging from 76% to 84%. The methoxy group in the 5-position was cleaved with a yield of 79% using hydrobromic acid to give the 5-hydroxy indole **8d**. Three trimethyl-*3H*-indoles (**8a, b, d**) were successfully transferred into tetramethyl-*3H*-indolium iodide salts (**3a-c**) in excellent yields >86% using iodomethane as both, solvent and reagent.

A method which had already been reported for the synthesis of 5-bromo indole was used to synthesize both, the 5-bromo (**8a**, 84%, Lit. 97%[30]) and 5-iodo (**8b**) precursor. The synthesis of the 5-iodo indolium salt **3b** has been reported earlier using different conditions which gave lower yields compared to our route (70%[31] and 74%[32]). The 5-hydroxy indolium salt **3c** was synthesized using a method previously reported.[14,18]

Further details (exact procedures, yields and analytical data) are provided in the supplementary material.



Scheme 4: Synthetic route to obtain indolium salts. a) 3-methyl-2-butanone; for X^1 = OMe: ethanol, reflux; for X^2 = Br, I: acetic acid, reflux. b) for X^1 = OMe: hydrobromic acid, reflux. c) iodomethane, reflux. Overall yields: X^1 = Br: 73%, X^2 = I: 73%, X^1 = OH: 56%.

2.2. Syntheses of Spiropyrans

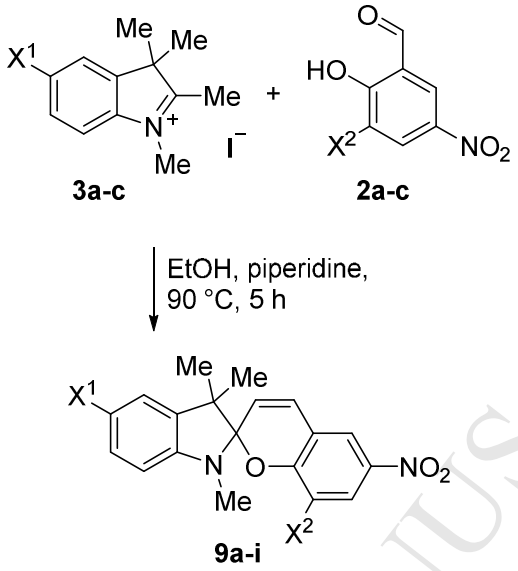
2.2.1. Spiropyran condensations

Spiropyrans were synthesized from indolium salts **3a-c** and salicylaldehydes **2a-c** using a versatile piperidine promoted procedure in ethanol as solvent (Table 1). The base was required to induce the *in situ* formation of 2-methyleneindolines (Fischer's bases) as reactive species from indolium salts **3**. For the synthesis of spiropyrans, the use of indolium salts is advantageous compared to directly using the corresponding Fischer's bases as starting materials, because indolium salts are stable against air and moisture and as solids easy to handle. All spiropyran products were obtained after crystallization from the reaction mixture. If necessary, they were further purified by recrystallization. The spiropyrans bearing either bromide, iodide or hydroxy functions showed a negative photochromism on silica gel. This means that they have ring opened to give the zwitterionic merocyanine isomer whose hydroxy groups can interact with the silica surface by hydrogen bonding leading to severe yield losses for the purification *via* column chromatography.[11]

The colors of the reaction mixtures and the corresponding isolated products were mostly dark brown, violet or blue. This suggested the presence of merocyanine species in the solid. We characterized the products using solution based techniques like NMR- or UV/vis-

spectroscopy and therefore could not determine the exact composition of the solids as synthesized. The spiropyrans' solvatochromism[6,33] was used to optimize the solvents for the NMR-characterization in order to obtain pure spectra of the closed or the corresponding open species, respectively.

Table 1: Synthesized spiropyrans. The starting materials **2a-c** and **3a-c** were used as equimolar solution in EtOH (17 mol/L), 2 eq. of piperidine were added and the solution was heated to reflux for 3-5 h.



Entry	Compound	X^1	X^2	Yield[a]
1	**9a**	Br	Br	78%
2	**9b**	Br	I	50%
3	**9c**	Br	OH	88%
4	**9d**	I	Br	79%
5	**9e**	I	I	62%
6	**9f**	I	OH	75%
7	**9g**	OH	Br	90%
8	**9h**	OH	I	83%
9	**9i**	OH	OH	98%[b]

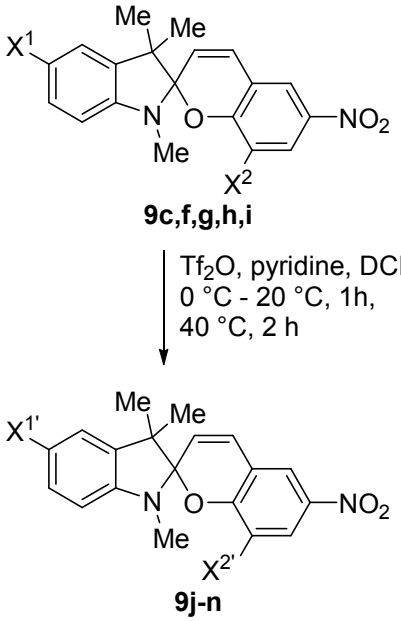
[a]The spiropyrans were obtained as solids and are likely mixtures of open and closed form.

[b]Reported yield: 99%.[14]

2.2.2. Transformation of Hydroxy Groups into Trifluoromethanesulfonyl Groups

The functionalization of the hydroxy groups to give the corresponding trifluoromethanesulfonyl groups was accomplished using trifluorosulfonyl anhydride as trifluorosulfonylating agent and pyridine as base in DCM as a solvent (Table 2). Under strict exclusion of oxygen and water, it was possible to obtain the five desired spiropyrans in good yields varying from 43% to 89%. The transformation of hydroxy groups into trifluoromethane-sulfonyl groups suppressed the inverse photochromism on silica gel. Therefore, it was possible to purify the spiropyrans with trifluoromethanesulfonyl groups using column chromatography or filtration through silica gel. Nevertheless, in the case of **9k** (Table 2, Entry 4), the binding of the merocyanine isomer to silica gel was noticeable resulting in a somewhat lower yield of 56%. The trifluoromethanesulfonyl groups at the indolene side of the molecule (**9l** and **9m**, entries 3 and 4) were obtained in lower yields, which is also due to their binding to silica gel. In the case of **9l**, a purification by chromatography was not possible. Therefore, several washing and precipitation steps were needed to remove pyridine and trifluoromethanesulfonic anhydride from the product. This also resulted in loss of yield.

Table 2: Introducing trifluoromethanesulfonyl groups into spiropyrans. Trifluoromethanesulfonyl anhydride (1.2 eq per OH group) was used as electrophile, pyridine (4 eq. per OH group) as base and DCM (0.25 mol/L) as solvent.



Entry	Compound	$X^{1'}$	$X^{2'}$	Yield[a]
1	**9j**	Br	OTf	74%
2	**9k**	I	OTf	56%
3	**9l**	OTf	Br	43%
4	**9m**	OTf	I	43%
5	**9n**	OTf	OTf	89%

[a]The spiropyrans were obtained as solids and are likely to predominantly consist of the open merocyanine form.

2.3. Sample Preparation for UV/vis and PSS Characterizations

A stock solution of each new spiropyran (100 mL, ca. 0.1 mmol/L) in acetonitrile was prepared. A defined volume (1 – 5 mL) was taken out of this solution and diluted to 10 mL to obtain the various desired sample concentrations (ca. 10 – 50 µmol/L).

The exact concentrations of the stock solutions are provided in the supplementary material.

For the determination of the ratio between spiropyran and merocyanine species in dark environment by ^{1}H NMR spectroscopy, 500 µL of the most concentrated solution (ca. 50 µmol/L) and 50 µL of deuterated acetonitrile were combined.

2.4. Photochromic Properties

All the synthesized spiropyrans were examined with respect to their photochromic properties. UV/vis spectra of all spiropyrans were measured while ensuring that measurements were taken in a concentration range in which the Beer-Lambert law is valid: Solutions of each spiropyran in acetonitrile were prepared in five different concentrations to obtain the absorption coefficients. This was done for the photostationary states after irradiation with visible and UV light (565 nm and 365 nm) as well as for the equilibria in the dark. The exact ratio (and thus, with the information of the total sample amount the concentration) of open and closed form in the dark was determined by ^{1}H NMR-measurements and used to calculate both, the molar absorption coefficient of the merocyanine form and its amount in the PSS^{365}.

The spectra and calculations for the diiodo functionalized dye **9e** will be described in greater detail as an example. All other spectra are provided in the supplementary material. Detailed information on the used UV-light and visible light irradiation sources are also provided there.

2.4.1. Photostationary State: Visible Light (λ = 565 nm)

Before the sample solutions were measured, the photochemical equilibrium between closed spiropyran and open merocyanine form was shifted towards the closed form by irradiation with visible light (λ = 565 nm) until the UV-vis spectra did not change anymore, which typically took about 30 seconds. For the determination of the absorption coefficient, solutions with five different concentrations in the range of 5 to 50 µmol/L of spiropyrans in acetonitrile were used. The spectra showed two major absorption bands, representing π-π* transitions in the indolene (~ 250 – 290 nm) and the chromene moiety (~ 300 – 350 nm).[33,34] In the

photostationary equilibrium under these conditions no merocyanine form was present[1] (which had a typical broad absorption band at ca. 500 to 600 nm).[6] Since only the chromene moiety contributes to a light yellow color of the solution, this absorption wavelength (in the case of **9e**: 314 nm, see Table 3 for all maxima values) could be used for the calculation of the molar extinction coefficient. Because these absorption spectra do not contain any significant absorption at wavelengths higher than 500 nm, no merocyanine form is present. An overview of the determined properties of all spiropyran dyes **9a-n** is provided in Table 3. A detailed description of the used analysis procedure and the plotted UV/vis spectra of the PSS^{565} and their concentration dependence are provided in the supplementary material.

2.4.2. Photostationary State: UV light (λ = 365 nm)

The solutions used in section 2.4.1 were irradiated with UV light (λ = 365 nm) until an equilibrium was reached, which typically took approx. 30 seconds. Plots of the obtained absorption spectra contain an absorption maximum at ca. 550 nm (For **9e**: 561 nm). Since the spiropyran form **9a-n^{SP}** does not absorb at wavelengths higher than 500 nm, the observed absorption maximum depends complety on the amount of merocyanine **9a-n^{MC}** present in the solution. A detailed description of the used analysis procedure and the plotted UV/vis spectra of the PSS^{365} and their concentration dependence are provided in the supplementary material.

2.4.3. Equilibrium in a Dark Environment

For all synthesized dyes **9a-n**, the PSS^{365} decayed with a half-life time for the decay of less than 30 minutes.[2] Therefore, it was not possible to directly determine the amount of merocyanine in the PSS^{365} via ^{1}H NMR spectroscopy. Due to the known formation of J- and H-aggregates by merocyanines,[6] increasing the concentration for faster NMR measurements was not an option.

[1] In the case of **9c** and **9f**, after irradiation with visible light, the solution contained a significant amount of the merocyanine species in the PSS.

[2] For the dyes **9g-k**, a decay measurement was not performed, because the concentration of merocyanine was lower at the PSS^{365} compared to dark conditions. This is because the merocyanine form also absorbs at this wavelength, leading to the formation of the spiropyran form, an effect that is not present in the dark equilibrium.

It was possible to measure the equilibrium between closed and open form which formed under dark conditions by both, UV/vis and ^{1}H NMR spectroscopy. The UV/vis solution or the NMR sample,[1] respectively, were kept dark for at least 24 h prior to the measurement. Following the earlier described procedure, it was possible to calculate the concentration dependence of the absorption maximum corresponding to the merocyanine transition (typically circa 550 nm). In the case of **9e**, it is 828 L(mol cm)$^{-1}$. By ^{1}H NMR spectroscopy, the ratio **9e^{MC}** / **9e^{SP}** was determined to be 4 / 96. For a comparison of the two species, the signals corresponding to protons of the ethylene bridge (*H*-3 and *H*-4) in the chromene moiety were used (Figure 2). These protons form doublets, with coupling constants of circa $^{3}J_{Z}$ = 10.5 Hz for **9e^{SP}** and $^{3}J_{E}$ = 16.5 Hz for **9e^{MC}**.

Thereby, the molar extinction coefficient of **9e^{MC}** was calculated as follows:

$$\varepsilon^{MC,561} = \frac{828}{4\%}\,\frac{L}{mol\ cm} = 20700\,\frac{L}{mol\ cm}$$

[1] A detailed procedure of sample preparation is provided in the supplementary material.

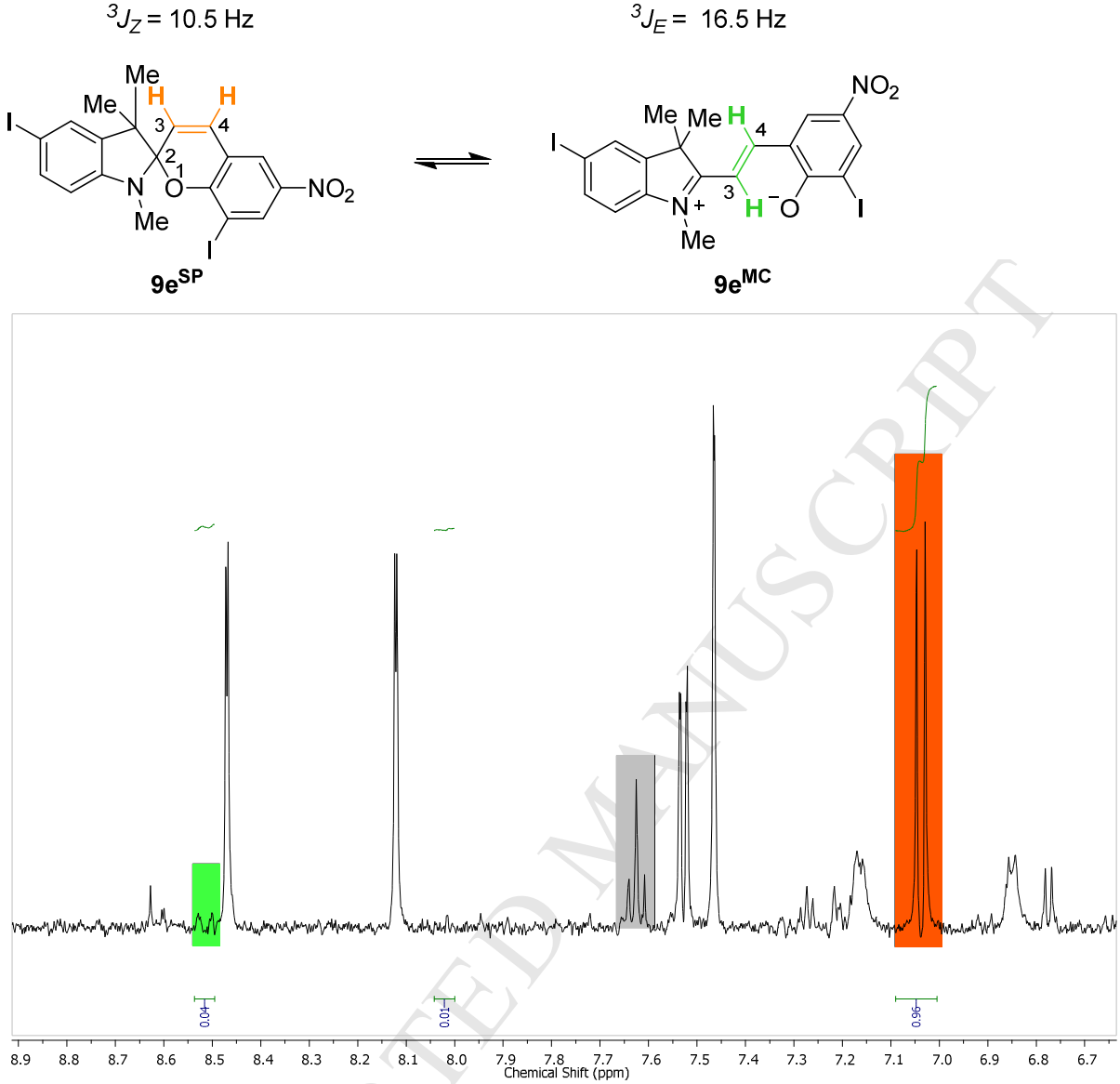


Figure 2: ^{1}H NMR spectroscopic determination of the ratio between **9e^{MC}** and **9e^{SP}** form in dark equilibrium. **a)** Structures of the species present in solution. The investigated protons are highlighted. **b)** Excerpt of the aromatic region of the ^{1}H NMR spectrum of the solution in acetonitrile after relaxation in dark environment for 24 h (sample concentration: 34 µmol/L). The specific protons are highlighted in orange (**9e^{SP}**) and green (**9e^{MC}**). Integration gives a ratio of 96 / 4. Grey boxes are used to mark residual impurities of deuterated acetonitrile. The third integral is used to determine the error of the integration. In this example, the integral of the baseline is 0.01.

2.4.4. Relaxation of the Photostationary States

Eventually, we also examined the relaxation of the photostationary states (Figure 3). To analyze the relaxation from the spiropyran from, the sample was irradiated at 565 nm to reach the photostationary state with enhancement of the spiropyran; then the light was switched off and the UV-vis spectra measured in dependence of the time. The absorbance at 561 nm, which corresponds to the absorption maximum increased with a half-life time of 8 min 51 s. The same procedure was used for analyzing the relaxation from the merocyanine form: irradiation at 365 nm to enhance the merocyanine concentration to equilibrium, switching off the light and recording the absorbance at 561 nm. The half-life time in this case was 13 min 21 s.

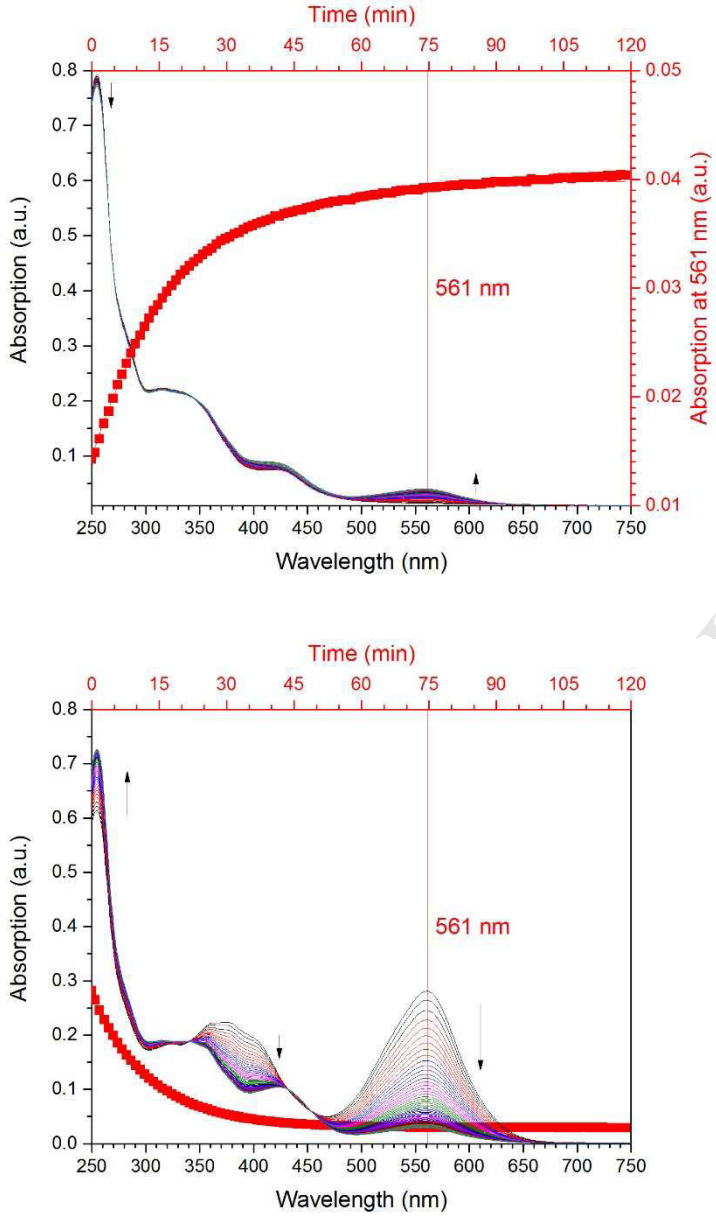


Figure 3: Relaxation of the **9e** system to an equilibrium (Sample concentration: 38 µmol in acetonitrile). Top: After stopping irradiation with green light (565 nm, until the photostationary state was reached), the merocyanine absorption at 561 nm increased with a half-life time of 8 min 51 s. bottom: Irradiation of the sample with UV light (365 nm, until the photostationary state was reached) enriched the merocyanine species. After removal of the illumination source, this was found to decay with a half-life time of 13 min 21 s.

3. Results and Discussion

The absorption spectra and photochromic properties of 13 formerly unknown spiropyrans were investigated. Table 3 contains the wavelengths of the absorption maxima of the π–π* transitions of the chromene and merocyanin moieties as well as the observed half-life times of the systems' relaxation from the photostationary states towards the equilibrium in dark. The π–π* transitions of the chromene moieties in the closed forms **9a-n^{SP}** vary between 304 nm (**9n^{SP}**; Table 3, entry 13) and 355 nm (**9c,f**; entries 3,6). As expected, a change of the substitution at this side of the molecule results in a large change of these absorption maxima. While bromide (**9a,d,g,l**; entries 1,4,7,11), iodide (**9b,e,h,m**; entries 2,5,8,12) and Trifluoromethylsulfonyl groups (**9j,k,n**; entries 9,10,13) at the chromene side show similar wavelengths between 304 and 320 nm, hydroxyl functions (**9c,f**; entries 3,6) result in a bathochromic shift with absorption maxima at wavelengths of 355 nm.

A similar trend can be found for the merocyanine transition with observed maximum wavelengths between 536 nm (**9j**; entry 9) and 570 nm (**9f**; entry 6). Again, a change in the substitution of the chromene side results in large changes of the absorption maxima's wavelengths. Trifluoromethylsulfonyl groups induce a hypsochromic shift of about 20 nm compared to bromide and iodide functionalities, whereas hydroxy groups induce a bathochromic shift of about 10 nm compared to the halide functionalities. Varying the substitution of the indole side (X^1) does not result in a larger change of the absorption wavelength. For example, compounds **9a,d,g,l** (entries 1,4,7,11) all bear a bromide as functional group at the chromene side, while the functional groups at the indole side vary: bromide (**9a**; entry 1), iodide (**9d**; entry 4), hydroxy (**9g**; entry 7), Trifluoromethylsulfonyl (**9l**; entry 11). The observed absorption wavelengths vary only between 547 (**9g**; entry 7) and 561 nm (**9l**; entry 7). For this absorption, hydroxy groups induce a hypsochromic shift, compared to the dyes with bromide or iodide at this position. Trifluoromethylsulfonyl groups at the indole side do not significantly influence the absorption maximum of the merocyanine transition significantly.

Relaxation of the systems after the PSS^{565} takes place with longer half-life times (08:51-285:32 min) than the relaxation after PSS^{365} (0:55-56:30 min). For 3 compunds (**9c,f,m**; entries 3,6,12), it was not possible to determine the half-life time, because the absorption spectra at the PSS^{565} and the equilibrium in dark are the same. The shortest half-life time was observed for compound **9e** (entry 5), which bears two iodide functionalities. Compounds with either hydroxy groups at the indole side (**9g,h**; entries 7,8) or trifluoromethylsulfonyl groups at the chromene side (**9j,k**; entries 9,10) show the slowest relaxation with half-life times ranging from 208 to 285 min. Two compounds with trifluoromethylsulfonyl groups at the chromene side (**9j,k**; entries 9,10) and two compounds with hydroxy groups at the indole side (**9g,h**; entries 8,9) could not be analyzed concerning their decay after PSS^{365}, because the amount of merocyanine was higher in the dark equilibrium. The other compounds with trifluoromethylsulfonyl or hydroxy groups show the fastest decay, with half-life times ranging from 55 sec (**9c**; entry 3) to 2:41 min (**9m**, entry 12). Most other relaxations show half-life times in the range of approx. 10-15 min, only the dye with two trifluoromethylsulfonyl groups (**9n**, entry 13) shows a significantly slower decay ($t_{1/2}$ = 56:30 min).

Table 3: Absorption maxima and half-life times from the photostationary states. In some cases, a half-life time could not be determined, as explained in the footnotes.

Entry	Compound	X^1	X^2	Absorption maximum[a]		Half-life time $t_{1/2}$ (min:sec)[a]	
				π-π* transition of chromene	Merocyanine transition	After PSS^{565}	After PSS^{365}
1	**9a**	Br	Br	315 nm	556 nm	23:07	15:21
2	**9b**	Br	I	306 nm	559 nm	22:16	11:28
3	**9c**	Br	OH	355 nm	568 nm	n.n.[b]	00:55
4	**9d**	I	Br	308 nm	559 nm	25:07	14:23
5	**9e**	I	I	314 nm	561 nm	08:51	13:21
6	**9f**	I	OH	355 nm	570 nm	n.n.[b]	01:12
7	**9g**	OH	Br	320 nm	547 nm	285:32	n.n.[c]
8	**9h**[d]	OH	I	320 nm	549 nm	271:45	n.n.[c]
9	**9j**	Br	OTf	308 nm	536 nm	253:17	n.n.[c]
10	**9k**	I	OTf	311 nm	538 nm	208:11	n.n.[c]
11	**9l**	OTf	Br	331 nm	561 nm	n.n.[b]	02:43
12	**9m**	OTf	I	335 nm	557 nm	n.n.[b]	02:41
13	**9n**	OTf	OTf	304 nm	537 nm	121:20	56:30

[a] In acetonitrile, concentrations ranged between 10 and 50 µmol/L.

[b] The absorption spectra of the PSS (565 nm) and of the equilibrium in the dark showed no differences.

[c] The concentration of merocyanine at the PSS (365 nm) was lower than the concentration of merocyanine in dark environment.

[d] Because the UV/vis spectrum of the highest concentration showed a strong deviation from the expected linear increase, only the four other concentrations were used for the calculation of molar absorbances.

For 13 spiropyran dyes **9a-n** we were able to determine the molar extinction coefficients of the merocyanine transitions (see **Table 4**). Therefore, the absorption at the equilibrium state in dark was plotted against the overall concentration. The obtained values range from 289 L(mol cm)$^{-1}$ (**9m**; entry 12) to 31621 L(mol cm)$^{-1}$ (**9g**; entry 7). While compounds with only halide functionalities (**9a,b,d,e**; entries 1,2,4,5) or trifluoromethylsulfonyl functional groups at the indole side (9l,m; entries 11,13) show low absorptions coefficients at approx. 1000 L(mol cm)$^{-1}$, hydroxy groups at the chromene side rise the absorption coefficients to approx. 2500 L(mol cm)$^{-1}$ (**9c,f**; entries 3,6). The introduction of hydroxy groups at the indole side increases the measured absorptions further to values of 15 or 30 kL(mol cm)$^{-1}$ (**9g,h**; entries 7,8). Transformation of hydroxy to trifluoromethylsulfonyl groups at the chromene side increases the absorption to approx. 20 kL(mol cm)$^{-1}$ (**9j,k**; entries 9,10). These absorptions originate solely from absorptions of the merocyanine species **9a-n^{MC}**. Thereby, the ratios **9^{MC}**:**9^{SP}** were determined by ^{1}H NMR spectroscopy under exclusion of light and could be used to calculate the molar extinction coefficients ε^{MC} of the merocyanine forms. These values range from 9327 L(mol cm)$^{-1}$ (**9b**; entry 2) to 54519 L(mol cm)$^{-1}$ (**9g**; entry 7).

The measured absorptions at the PSS^{365} were divided by the calculated molar extinction coefficients to obtain the ratio [MC]:[SP]. Three compounds (**9a,b,m**; entries 1,2,12) show a complete switch. For the other compounds, the amount of **9^{MC}** is between 3 and 88%. The four compounds which had the highest molar absorption in the dark show significantly lower absorptions at the PSS^{365} and thereby a smaller proportion of **9^{MC}** is present (3-19%; **9f-k**; entries 6-10).

Table 4: Determination of the molar extinction coefficient of merocyanine and the merocyanine: spiropyran ratio at the PSS (365 nm). A table showing errors of the ^{1}H NMR integration and resulting errors of the other properties is provided in the supplementary material.

Entry	Compound	Equilibrium in dark environment			PSS (365 nm)	
		Molar absorption (L(mol cm)$^{-1}$)	Ratio [MC]:[SP]	ε^{MC} (L(mol cm)$^{-1}$)	Molar absorption (L(mol cm)$^{-1}$)	Ratio [MC]:[SP]
1	**9a**	1858	08:92	23225	30591	100:0[a]
2	**9b**	1082	12:88	9327	11500	100:0[a,b]
3	**9c**	2424	07:93	34628	27520	79:31
4	**9d**	1576	07:93	22514	19770	88:12
5	**9e**	828	04:96	20700	8320	40:60
6	**9f**	2209	06:94	36817	24215	66:34
7	**9g**	31621	58:42	54519	1747	03:97
8	**9h**	15851	56:44	28305	1972	07:93
9	**9j**	21876	59:41	37078	6885	19:81
10	**9k**	23936	52:48	43031	5274	11:89
11	**9l**[c]	336	02:98	16800	24402	100:0[d]
12	**9m**	289	16:84	1806	6292	100:00[d]
13	**9n**	6879	27:73	25477	11532	45:55

[a] The calculated ε^{MC} led to an apparent amount of more than one equivalent of merocyanine in the PSS^{365}, which is due to an integration error in this ^{1}H NMR spectroscopic measurement of ± 0.01. However, the observed extinction coefficient in the PSS is included in the error ranges. Plots of all NMR spectra including integrals and a detailed table with errors are provided in the supplementary material.

[b] A different proton signal was used for integration, due to an overlap of the ethylene protons of the merocyanine species

[c] Due to very low total absorptions of the merocyanine transition, it was necessary to use concentrations from 60 to 100 µmol/L for UV/vis and ^{1}H NMR spectroscopy.

[d] The calculated ε^{MC} led to an apparent amount of more than one equivalent of merocyanine in the PSS^{365}. The measured absorptions in the dark were close to the device's detection limits.

4. Conclusion

Thirteen novel spiropyran dyes were synthesized and characterized in terms of their UV/vis spectra and their switching properties. Eight of these dyes were synthesized in good to excellent yields (50-90%) by condensation reactions. In addition, a versatile method (five examples) was established that gives access to trifluoromethane sulfonyl groups as functionalization of spiropyrans in good yields (56-89%). Importantly, the functional groups that were introduced (I, Br, OTf) are all highly suitable for cross-coupling reactions, enabling access to spiropyrans functionalized with unsaturated groups which was not possible before. Owing to the combination of halide with/and hydroxyl functionalities on the molecules, condensation reactions with the hydroxyl groups can be performed on one end of the molecule, whereas the halide gives access to cross-coupling based extensions of the spiropyran scaffold. The decay times of the photostationary states at the absorption maxima merocyanine (365 and 565 nm) were determined and vary between 55 seconds and 56 minutes for 365 nm and between 9 minutes and 285 minutes for 565 nm. It was possible to determine the amount of merocyanine in the photostationary states (365 nm) (3-100%) by applying a combined UV/vis and ^{1}H NMR spectroscopic analysis. This method also allowed us to calculate the molar extinction coefficients of the merocyanine species (9.3-25 k(L(mol cm)$^{-1}$)). Work is ongoing to establish selective cross-coupling procedures for this new library of spiropyrans.

Supplementary Material

Supplementary material includes: purities of the reactants and reagents used, drying procedures for the solvents; synthetical and analytical equipment; experimental procedures and ^{1}H and ^{13}C {^{1}H} NMR spectra for all synthesized compounds; UV/vis spectra for all new spiropyrans ($PSS_{365\ nm}$, $PSS_{565\ nm}$, dark), determination of decay times and molar extinction coefficients using a combination of UV/vis and ^{1}H NMR spectroscopy.

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